Time-dependent, irreversible entropy production and geodynamics

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We present an application of entropy production as an abstraction tool for complex processes in geodynamics. Geodynamic theories are generally based on the principle of maximum dissipation being equivalent to the maximum entropy production. This represents a restriction of the second law of thermodynamics to its upper bound. In this paper, starting from the equation of motion, the first law of thermodynamics and decomposition of the entropy into reversible and irreversible terms,1 we come up with an entropy balance equation in an integral form. We propose that the extrema of this equation give upper and lower bounds that can be used to constrain geodynamics solutions. This procedure represents an extension of the classical limit analysis theory of continuum mechanics, which considers only stress and strain rates. The new approach, however, extends the analysis to temperature-dependent problems where thermal feedbacks can play a significant role. We apply the proposed procedure to a simple convective/conductive heat transfer problem such as in a planetary system. The results show that it is not necessary to have a detailed knowledge of the material parameters inside the planet to derive upper and lower bounds for self-driven heat transfer processes. The analysis can be refined by considering precise dissipation processes such as plasticity and viscous creep.

Keywords: limit theorems; plasticity theory; finite-time thermodynamics; irreversible entropy; Carnot efficiency; endoreversible engine

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1The equality form of the second law and the decomposition of entropy are due to Tolman & Fine (1948).

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1. Introduction

The title of our paper was chosen in honour of the excellent contribution by Tolman and Fine as published in their 1948 paper ‘On the irreversible production of entropy’. Tolman and Fine highlighted that a distinction must be made between the entropy change due to entropy crossing the boundary between the system and surroundings and the entropy generated inside the system through irreversible processes. The total production of entropy is hence equal to the change of entropy from entropy transfer through the system owing to reversible processes (reversible entropy change) plus the entropy generated through dissipative processes inside the system (irreversible entropy production). This is known as the entropy balance law of Tolman and Fine, which recasts the second law of thermodynamics in a mathematically more convenient equality form. In this paper, we clearly distinguish entropy production from entropy change and discuss the resultant minima and maxima of the entropy production in an example of a planet seen as a heat engine. Furthermore, we hypothesize that the minimum and maximum irreversible entropy production can be used as an abstraction tool to understand basic modes of geodynamic processes and derive a novel formulation for calculating the upper and lower bounds.

Entropy production can be directly related to the dissipation caused by irreversible processes. Although the number of dissipative processes may not be tractable in the Earth, classical approaches use only an upper bound provided by the principle of maximum dissipation for an assumed set of processes (Ziegler 1983). A lower bound can also be calculated and thermal feedbacks can be taken into consideration. The advantage of calculating both the upper and lower bounds is that we can predict basic planetary behaviour without going into specific modelling of the underlying physics. We suggest that extremum principles in this context are an extremely useful first pass before embarking on laborious modelling of complex geodynamic processes.

Earlier work on this subject comes from the chemical modelling or the climate modelling community focusing either on the minimum (Glansdorff et al. 1973) or on the maximum principle of entropy production (Paltridge 1979). Although these approaches allow very elegant solutions to complicated problems in Earth sciences (Ozawa et al. 2003), they are nonetheless entirely based on minimum/maximum assumptions about how a thermodynamic system should behave. No reasons are given why the thermodynamic system should behave one way or the other. We show that a natural fluid dynamic heat transfer system is described by a minimum of entropy production defined by Fourier’s Law of conduction and derive an expression for increased production of entropy upon the onset of convection. We introduce a non-dimensional number to characterize steady-state entropy production rate. The arguments are derived from the classic paper of Tolman & Fine (1948) but here we leave out their explicit incorporation of chemistry. The concepts summarized in the first half of the paper are classical and are described in detail in textbooks of thermodynamics and continuum mechanics. We realize that many details of this classical material may be foreign to the geodynamicist. For the sake of brevity, we provide a short review and refer to the literature for in-depth reading on concepts such as the principle of virtual work or incomplete differentials.

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2. Energy balance

Classical continuum mechanics is based on physical laws that are cast in such a way that energy flows are compatible with the first and second laws of thermodynamics. The fundamental notions of conservation of energy and increase in entropy are hence firmly embedded in a mechanical process. We consider a representative volume element (RVE) subjected to external loads. A RVE is a set of material points with defined properties that are statistically invariant with respect to volume when the volume is upscaled. The application of the principle of virtual power (Lemaitre & Chaboche 1994) results in

$$\mathcal{P}_{\text{int}} + \mathcal{P}_{\text{ext}} = \mathcal{P}_{\text{acc}}, \quad (2.1)$$

where the internal power, $\mathcal{P}_{\text{int}}$, is the product of the generalized stress, $B_{ij}$, with the generalized strain rate, $v_{ij}$, integrated over the RVE. The generalized stress (Houlsby & Puzrin 2007) corresponds to a thermodynamic force and the generalized strain rate corresponds to a thermodynamic flux. In a typical geodynamic problem, where volumetric deformation is neglected, these generalized stresses and strain rates are the classical deviatoric stresses and deviatoric strain rates; however, they can have a much wider application. The thermodynamic force can, for instance, be a pressure difference, a temperature difference, a difference in chemical potential, electrical potential, etc. (Onsager 1931). The conjugate thermodynamic fluxes can be a volume change, a heat change, a change in chemical species, electrical current, etc. This internal power is balanced by the virtual power of the exterior and inertial forces $\mathcal{P}_{\text{ext}}$ and $\mathcal{P}_{\text{acc}}$, respectively. Applying the first law of thermodynamics gives

$$\frac{d}{dt} \int_V \rho u \, dV = \dot{W} + \int_V r_i \, dV - \int_{\partial V} q \cdot n \, d\Gamma, \quad (2.2)$$

where $u$ is the specific internal energy, $q$ is a heat flux vector, $n$ is a normal vector to the surface, $\Gamma$, of the RVE and $\dot{W} = \int B_{ij} v_{ij} \, dV$ is the rate of change of total work. We use the Einstein tensor notation and the ‘tilde’ for the work rate to emphasize that time integrals are path dependent (Callen 1985). This is the classic linear irreversible thermodynamic formulation in the case of thermo-mechanical, quasi-static equilibrium. More details can be found in Regenauer-Lieb et al. (2009). The source term, $r_i$, is a discrete summation which collects the rate of heat production (e.g. radioactive decay, Joule heating and chemical reaction) inside the RVE. This additional source term has been criticized (Houlsby & Puzrin 2007). The term $r_i$ is only necessary as an ‘artificial’ source term in the energy equation if the effect on the internal energy is not resolved by the thermodynamic calculation. The source term would not be necessary if the change in isotopes through radioactive decay or chemical changes or electrical currents inside the RVE are explicitly resolved or calculated in a full equation of state.

Therefore, incorporating equations (2.1) and (2.2), Gauss’ theorem, the conservation of mass and the assumption of an arbitrary $V$, at the local level we obtain the energy rate equation for the RVE in thermal–mechanical, quasi-static equilibrium as

$$\rho \dot{u} = B_{ij} v_{ij} + r_i - \text{div} \, q, \quad (2.3)$$
where the over dot identifies the material time derivative. This description of the internal energy balances out the mechanical and thermal energies coming from the mechanically induced heat source contribution from $B_{ij}v_{ij}$ in quasi-static equilibrium, with the additional solution-strategy-dependent term $r_i$ and heat fluxes.

3. Limit theorems in continuum mechanics

In classical continuum mechanics, solutions to quasi-static deformation are sought where time-dependent thermodynamic fluxes have relaxed to quasi-static equilibrium. Time dependency, which follows from the feedback of temperature, material behaviour and deformation, is not considered in the basic framework. The thermodynamic conditions for quasi-static equilibrium were first suggested in general plasticity theory (Hill 1951; Rice 1971). This work was generalized to a wide range of thermo-mechanical processes by the postulate of maximum rate of dissipation, which is also known as the maximum entropy production principle (Ziegler 1983). For such time-independent solutions, upper and lower bounds of the energy required to deform a solid can be obtained from limit theorems described next.

Limit theorems in continuum mechanics were originally put forward for solving three groups of differential equations of a non-hardening plastic–rigid material. These are the stress equilibrium equations, the stress–strain relations and the equations relating strain and displacement. There is no unique solution to the elasto-plastic problem for the plastic material under consideration. An infinity of statically admissible stress states will satisfy the stress boundary conditions, the equilibrium equations and the yield criterion alone. In addition, an infinite number of virtual kinematically admissible displacement modes will be compatible with a continuous distortion satisfying the displacement boundary conditions (Bishop 1953). Therefore, one has to be satisfied with partial or incomplete solutions for which limit theorems have been put forward to provide assessment of the predicted yield-point loads (Hill 1951). Yield-point load is an engineering term to describe the capacity of a structure or material to support external forces.

**Lower bound theorem:** The yield-point loads are determined from a distribution of stress that satisfies the equilibrium equations and stress boundary conditions and nowhere violating the yield criterion.

**Upper bound theorem:** The yield-point loads, determined by equating the external work to the internal work done in a deformation mode satisfying the displacement boundary conditions by that stress distribution needed to enforce those conditions at each point, are not less than the actual yield-point loads. The displacement is not necessarily the actual displacement of the deforming body but virtual displacement used to calculate the upper bound. The constraint on these displacements is that they are ‘kinematically admissible’ with respect to the boundary conditions. The stress distribution need not be in equilibrium and is defined only where the strain rate is non-zero. In other words, the upper bound considers only the dissipative part of the deformation process, which according
to Ziegler’s principles uses maximum entropy production as a thermodynamic consistency check. The limit theorems do not, however, involve in themselves an explicit thermodynamic treatment.

These theorems have since proven invaluable for engineering calculations of a wide field of rheologies and have been extended over a wide range of applications (Salencon 2002). They provide sound estimates for the upper and lower bounds of energy required to deform solids. We propose here that an extension to the entropy balance will provide similar use in geodynamics.

4. Entropy balance

Geodynamic problems are inherently irreversible and time dependent. We define the entropy production, in accordance with Tolman & Fine (1948, eqn (18.4)), by

$$\dot{S} = \int_V \frac{r_i}{T} dV - \int_{\partial V} q T \frac{n}{T} d\Gamma + \dot{S}_{irr}. \quad (4.1)$$

Hence, the internal irreversible entropy generation collects the thermo-chemical dissipative sources. With this definition of the entropy, a local form can be obtained in an analogy with the derivation of energy equation (2.3)

$$\rho T \dot{s} = \rho T \dot{s}_{irr} + r_i - T \text{div} \left( \frac{q}{T} \right), \quad (4.2)$$

where $\dot{s}$ is the total specific entropy change rate in the local form, $\dot{s}_{irr}$ is the path-dependent irreversible specific entropy production rate and $T$ the absolute temperature. We recognize the first term on the right-hand side as the entropy production caused by mechanical, chemical, radioactive and electrical process contributions, which must be positive or zero according to the second law of thermodynamics. By the additional constraint that the absolute temperature $T > 0$, the entropy balance law encapsulates the entire system of classical laws of thermodynamics (Bonetti et al. 2005). The third term is the total entropy flux, which homogenizes the entropy change rate. This concept of writing the second law of thermodynamics in an equality form and the point that the entropy rather than the temperature describes the underlying physical processes are fundamental points of Tolman & Fine’s (1948) classic paper.

5. Minimum and maximum entropy production

Consider a thermodynamic system that from an initial time $t_{\text{init}}$ reaches a given final state in time $t_{\text{fin}}$. We assume that this final state may be relaxed to an equilibrium state, or it may be a steady state, which can be sustained only by an internal dissipation process.

We identify two extrema that relate to whether the entire system reaches equilibrium (minimum entropy production) or whether it is in a cyclical, quasi-static, steady state, which could be sustained by an internal dissipation process (entropy production is not necessarily a minimum). The important role of entropy production was proposed by Tolman & Fine (1948) in their eqn (5.1).
We reformulate their arguments that allow changes in internal temperature through time. For this we invoke the Helmholtz formulation of the internal energy

\[ u = \psi + sT, \quad (5.1) \]

where \( \psi \) is the specific Helmholtz free energy dependent on the state variables. We differentiate equation (5.1) with respect to time and obtain

\[ \dot{u} = \dot{\psi} + \dot{s}T + \dot{T}s. \quad (5.2) \]

According to equations (2.1) and integrating equation (5.2), we can formulate an efficiency equation for the thermodynamic system. This efficiency is defined as the total amount of recoverable power

\[ \dot{J} = \int (\partial \dot{\psi}/\partial \alpha_{ij}) \dot{\alpha}_{ij} \, dV \]

that can be stored in the thermodynamic system, where \( \partial \alpha_{ij} \) describes all recoverable state variables, like elastic strain, and \( \partial \) delineates an incremental change of the state variable. This stored power is limited by two bounds

\[ \dot{J}_{\text{max}} = \max \left[ \tilde{W} - \left\{ \int_{V} \frac{q \cdot \text{grad}(T)}{T} \, dV + \int_{V} \rho T \tilde{s}_{\text{irr}} \, dV \right\} \right] \quad (5.3) \]

and

\[ \dot{J}_{\text{min}} = \min \left[ \tilde{W} - \left\{ \int_{V} \frac{q \cdot \text{grad}(T)}{T} \, dV + \int_{V} \rho T \tilde{s}_{\text{irr}} \, dV \right\} \right]. \quad (5.4) \]

If we attribute the irreversible entropy to the plastic dissipation, assume Ziegler’s principle of maximum dissipation and ignore the temperature feedback terms encapsulated in the time derivative of the irreversible entropy production (Regenauer-Lieb et al. 2009), equation (5.4) reverts to the classical upper bound principle. The classical lower bound considers only the work and neglects effects of temperature and time derivatives. Our formulation extends this by adding the second and third term in equation (5.3). Therefore, we hope to be able to extend the yield design theory underpinned by the limit theorems in continuum mechanics (Salencon 2002) for discrete examples in the future. Also, if we assume the temperature of the environment \( T_{\text{surf}} \) to be constant, we can use an explicit open system formulation and from integrating equation (5.3) over finite time we recover the basic equation for finite-time thermodynamics (Andresen et al. 1984).

Note that the analogy of the limit theorems in terms of work can only be cast rigorously into a limit theorem of dissipated power and not integrated for work. The integration of equation (5.3) or (5.4) is only possible over finite time for specific classes of thermodynamic problems such as cyclical or steady-state problems as shall be discussed below.

6. Limit theorems in geodynamics

The above considerations of minimum/maximum work or maximum/minimum entropy production, respectively, apply to engineering applications where we may apply some kind of engineering design (e.g. optimal control theory) to achieve a desired goal. The approach lends itself to immediately extend the limit theorems of continuum mechanics to a time-dependent process.
We are left with the discussion of how meaningful an extrapolation of the entropy production extrema and the related upper and lower bounds is for geodynamics. We do not answer the critical question whether nature really seeks an extremum in quasi-steady state, but instead we discuss the merits of the extremum principles using the insights from thermodynamics to provide upper and lower bounds to general deformation processes that must not be violated. We also show the sensitivity of the solution of entropy production at the large-scale boundaries of our system and inside the system. From these examples, it will become clear that we need to consider the explicit role of entropy production for time-dependent deformation processes such as models of mantle convection.

We now discuss a simple cyclical dissipative system for which the efficiency equations (5.3) and (5.4) can be integrated over finite time. Note that this integration of the weak form is not universally valid for any thermodynamic process since work and heat are imperfect differentials. We can integrate by considering a temperature $T_0$ as the temperature of the environment (which in our case is chosen to be the surface temperature of the Earth) as an additional constraint. We reformulate equations (5.3) and (5.4) in the strong form and obtain the following formulation for the recoverable (elastic) energy rate

$$\dot{J} = \tilde{W} - \int_V \left( \frac{T - T_0}{T_0} \right) \text{div} q \, dV - \int_V \left( \frac{T - T_0}{T_0} \right) T_0 \dot{\delta} \, dV$$

$$- T_0 \int_V \frac{q \cdot \text{grad}(T)}{T^2} \, dV - \int_V \rho T_0 \dot{s}_{\text{irr}} \, dV,$$

where $\tilde{W}$ is the total work rate, the second term on the right-hand side identifies the equivalent work rate generated due to the net heat input at $T$, the third term is the equivalent work rate consumed to upgrade the entropy change rate of the system from $T_0$ to $T$ and the last two terms are the irreversibilities due to heat transfer and chemo-mechanical processes, respectively. Thermodynamicists will recognize the second term as the work of a Carnot engine and the third term as the work of a Carnot refrigerator. The strong formulation for the recoverable power in equation (6.1) is valid for any thermodynamic system relaxing to cyclic or steady-state equilibrium, although the following example considers only a restrictive cyclical process. In particular, equation (6.1) is valid for chaotic heat transfer process as long as a continuum formulation is valid.

For finite-time integration, we assume that during each cycle there is no net change of the recoverable work through change in state variables $\partial \alpha_i$ like the elastic strain or similar and $\dot{J} = 0$. Also, the Carnot refrigerator work term is zero under cyclic steady state. The system is driven only by the amount of heat absorbed per cycle $Q$. The fourth term on the right-hand side of equation (6.1) is non-zero for heat transfer in a spherical Earth; however, for a linear temperature profile problem it is zero. Equation (6.1) can then be integrated to yield the following expression:

$$W = \frac{T_{\text{core}} - T_{\text{surf}}}{T_{\text{core}}} Q - T_0 \Delta S_{\text{irr}}.$$
By way of this Carnot analogy (Pons & Le Quere 2005), the maximum efficiency of the Earth’s heat engine is the theoretical maximum Carnot limit $\eta = (T_{\text{core}} - T_{\text{surf}})/T_{\text{core}} = 1 - T_{\text{surf}}/T_{\text{core}}$, where the temperature of the environment is $T_0 = T_{\text{surf}}$ being the surface temperature and $T_{\text{core}}$, the temperature at the core–mantle boundary. Assuming in equation (6.2) that the irreversible entropy production is at its absolute minimum, i.e. zero valued, it follows that the reversible entropy production defined by the first term on the right-hand side cannot be above this limit and therefore it defines a theoretical upper bound of the amount of work that can be extracted from efficiency equation (6.1). In the next section, we will develop a generalized interpretation of equation (6.1) in terms of minimum and maximum entropy production between two surfaces.

7. Upper and lower bounds of dissipation to self-driven heat transfer phenomena

The thermodynamic upper and lower bounds to self-driven heat transfer phenomena between two surfaces at dissimilar temperatures can be indexed by a non-dimensional entropy generation number introduced here. For obtaining bounds to a quasi-incompressible medium, we revisit equation (6.1) and define a measure of dissipation $\tilde{H}$, which is also known as the rate of lost work for the case of the linear temperature gradient. A minimum in the dissipation corresponds to a minimum in irreversible processes of the system and surroundings

$$\tilde{H} \equiv \int_V \left( \frac{T - T_0}{T_0} \right) T_0 \tilde{s} \, dV + \int_V \rho T_0 \tilde{s}_{\text{irr}} \, dV + j - \tilde{W}. \quad (7.1)$$

In the limit with zero irreversible entropy production discussed in the example for equation (6.2), the first term on the right-hand side would equate to the rate of work extracted from the engine and the second and third terms of equation (7.1) are zero. The minimum possible dissipation defined in equation (7.1) would be $\tilde{H} = 0$.

In the following equations, we develop a general formulation for extrema of dissipation, which can be derived from equation (7.7). It follows from equation (6.1) that

$$\tilde{H} = - \int_V \left( \frac{T - T_0}{T} \right) \text{div} q \, dV - T_0 \int_V \frac{q \cdot \text{grad}(T)}{T^2} \, dV. \quad (7.2)$$

Consider an Earth where we have only observations available at the surface and do not know whether conduction or convection occurs. We assume boundary layers to be outside of our system. We have to consider two possible cases of heat transfer, which are considered in parallel, conduction and convection (figure 1). The case where all heat transfer is given by conduction and no convection occurs is the minimum entropy production case. Using Green’s lemma, equation (7.2) can be written as

$$\tilde{H} = - \int_F q \cdot n \, dF + T_0 \int_F \frac{q}{T} \cdot n \, dF. \quad (7.3)$$
Integration of this equation yields
\[ \tilde{H} = (Q_{\text{core}} - Q_{\text{surf}}) + \frac{T_0}{T_{\text{surf}}} Q_{\text{surf}} - \frac{T_0}{T_{\text{core}}} Q_{\text{core}}, \] (7.4)
where \( Q_{\text{core}} \) and \( Q_{\text{surf}} \) are the heat quantities transferred at the core and the surface, respectively, and \( T_{\text{core}} \) and \( T_{\text{surf}} \) are the corresponding temperatures.

We define a non-dimensional dissipation number \( \zeta \) to normalize the lost work rate \( \tilde{H} \)—which has dimensional units of heat—with respect to the conductive heat as follows:
\[ \zeta \equiv \frac{\tilde{H}}{Q_{\text{cond}}}. \] (7.5)

Rearranging equation (7.4) and considering that \( T_{\text{surf}} = T_0 \), it follows that
\[ \zeta = \frac{Q_{\text{core}}}{Q_{\text{cond}}} \left(1 - \frac{T_0}{T_{\text{core}}} \right). \] (7.6)

Using the classical definition of the Nusselt number \( Nu \) (convective over conductive heat transfer) as well as the Carnot efficiency, the dissipation number for any internal temperature profile is
\[ \zeta = Nu \left(1 - \frac{T_{\text{surf}}}{T_{\text{core}}} \right) = Nu \eta. \] (7.7)

Extrema of the above equation give a very interesting interpretation of the possible mode of dissipation inside a planetary system. The minimum of \( \zeta \) is the case where the Nusselt number \( Nu \rightarrow 1 \). This is the purely conductive case, which implies a minimum of the reversible entropy change. The other extremum corresponds to the maximum of \( \zeta = Nu_{\text{max}} \eta \). If material properties are known this limit can be obtained from equation (7.1) and hence \( Nu_{\text{max}} \) can be derived.
The upper limit on entropy production can, however, be changed if we consider the inclusion of radiogenic heat production at arbitrary locations inside the mantle.

8. Introduction of radiogenic heat

Radiogenic heat production at arbitrary locations inside the mantle is considered here with the following constraints:

\[
\begin{align*}
\frac{Q_{\text{surf}}}{T_{\text{surf}}} &= \frac{Q_{\text{core}}}{T_{\text{core}}} + \frac{Q_{\text{rad}}}{\hat{T}_{\text{rad}}}, \\
\frac{1}{T_{\text{surf}}} &= \frac{\Phi}{T_{\text{core}}} + \frac{1 - \Phi}{\hat{T}_{\text{rad}}},
\end{align*}
\]

(8.1)

where \( \hat{T}_{\text{rad}} = \int_V r_i \text{d}V / \int_V \text{d}V \) is the effective temperature stemming from the normalization of integration of the radiogenic heat term \( r_i \) over the mantle to deliver the radiogenic heat term \( Q_{\text{rad}} \) and substituting \( \Phi = Q_{\text{core}} / Q_{\text{surf}} \). The second constraint is that

\[
\tilde{W} = Q_{\text{surf}} + Q_{\text{core}} + Q_{\text{rad}}.
\]

(8.2)

We define the equivalent Nusselt efficiency for the case of the three heat components

\[
\eta_{3C} = \frac{\tilde{W}}{Q_{\text{core}} + Q_{\text{rad}}}
\]

(8.3)

and obtain

\[
\eta_{3C} = 1 - \frac{T_{\text{surf}}}{T_{\text{core}}} \Phi - \frac{T_{\text{surf}}}{\hat{T}_{\text{rad}}} (1 - \Phi)
\]

(8.4)

replacing \( \eta \) in equation (7.4). The mathematical results can be visualized with the aid of classical \( T-S \) diagrams (figure 2). These diagrams are used in thermodynamics as an engineering design tool to derive the amount of extractable work in the engine cycle. Engines have a clockwise path, while refrigerators have an anticlockwise path. We consider only clockwise engines. Vertical lines represent reversible adiabatic (isentropic) processes, while oblique lines show irreversible adiabats. Both processes are assumed to happen fast enough as to involve only changes in temperature without addition or loss of heat with the surroundings. Note that work can be extracted only along adiabats. There is a reduction in work extraction along irreversible adiabats until a critical angle is hit at which point zero work can be extracted. This case is illustrated in figure 2a. We refer to standard engineering textbooks for further details on interpreting \( T-S \) diagrams (Cengel & Boles 2007).

9. Application of limit analysis to a Cartesian Earth model

By way of example, assume that at the largest scale of geodynamic simulations the Earth is a heat engine where mantle convection performs a generalized engine cycle. We assume here that all the mechanical work done that drives plate tectonics is converted into heat in the interior of the Earth. We also assume that
Figure 2. Maximally dissipative modes of self-driven heat transfer from the core–mantle boundary to the surface with an affiliated lost work given by $\eta_2 C Q_{\text{cond}} + \eta_3 C (Q_{\text{core}} + Q_{\text{rad}})$, where $\eta_2 C = 1 - \frac{T_{\text{surf}}}{T_{\text{core}}}$ is the two-reservoir Carnot efficiency and $\eta_3 C = 1 - \Phi \frac{T_{\text{surf}}}{T_{\text{core}}}$ - (1 - $\Phi$) $\frac{\hat{T}_{\text{rad}}}{T_{\text{rad}}}$ is the three-reservoir Carnot efficiency, where $\Phi$ is defined as $\frac{Q_{\text{core}}}{Q_{\text{core}} + Q_{\text{rad}}}$ and $\hat{T}_{\text{rad}}$ defined as $\int V \dot{r} \, dV / \int V (\dot{r}/T) \, dV$. (a) A maximally dissipative heat engine that generates zero work with a concomitant conduction heat leak path. $Q_{\text{core}}$ or the heat received from the core–mantle boundary and $Q_{\text{rad}}$ or the heat received from radioactive decays are totally transmitted through viscous dissipation and internal heat transfer dissipation as $Q_{\text{surf}}$ so that the total amount of heat appearing at the surface is $Q_{\text{core}} + Q_{\text{rad}} + Q_{\text{cond}}$. Note that the area of the rectangle a–b–i–j, i.e. $Q_{\text{core}}$, plus the area of the rectangle c–d–g–h, i.e. $Q_{\text{rad}}$, is equal to the area of the rectangle e–f–k–l or $Q_{\text{surf}}$. Process paths b–c, d–e and l–a are adiabats. (b) A partially dissipative heat engine that generates work with a concomitant conduction heat leak path. $Q_{\text{surf}}$ is now less than $Q_{\text{core}} + Q_{\text{rad}}$, and the resulting work or $W$ is dissipated as heat at the surface through shearing action, so that the total amount of heat appearing at the surface is still equal to $Q_{\text{core}} + Q_{\text{rad}} + Q_{\text{cond}}$. Note that the area of the rectangle a–b–i–j, i.e. $Q_{\text{core}}$, plus the area of the rectangle c–d–g–h, i.e. $Q_{\text{rad}}$, is larger than the area of the rectangle e–f–k–l or $Q_{\text{surf}}$. Process paths b–c, d–e and l–a are adiabats. (c) A three-reservoir Carnot heat engine that generates maximum work with a concomitant conduction heat leak path. $Q_{\text{surf}}$ is the minimum heat rejection by the engine as dictated by the second law and $W$ is dissipated as heat at the surface through shearing action, so that the total amount of heat appearing at the surface is $Q_{\text{core}} + Q_{\text{rad}} + Q_{\text{cond}}$. 

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the Earth is a Cartesian box with a perfectly flat surface (no potential energy change at the surface). This concept describes a certain class of computer models of mantle convection where heat is supplied and extracted at the boundaries and internal irreversible losses through radioactive decay are neglected. Similarly, all irreversible losses attributed to coupling of the Earth to its environment are neglected.

Both minimum entropy production cases are trivial: case I is an isothermal Earth, when $T_{\text{core}} \to T_{\text{surf}}$, and case II is the Earth as a purely conductive medium. Both cases are obviously not very attractive for a realistic Earth model.

The maximum upper bound of an irreversible engine—not necessarily a Carnot engine—is given by three engines with three heat reservoirs. The first two realizations are illustrated in figure 2a,b as irreversible heat engines. The third realization in figure 2c, which includes an arbitrary internal radiogenic heat source, involves a Carnot heat engine that is constructed to deposit its work into shear heating at the surface. Figure 2c is an interesting case. While depositing the work as shear heating at the surface may not be very realistic, if instead the work were deposited at the lithosphere–asthenosphere boundary the idealized Carnot analogy may be a very good zero-order approximation to mantle convection. In summary, all three maximum entropy production cases are more attractive solutions than the lower bound. The solutions show the necessity of explicitly calculating the conversion of mechanical work into heat in any mantle convection problem. We now turn to a more quantitative analysis.

Assume a core–mantle boundary temperature between 4500 and 3600K (Knittle & Jeanloz 1991; Hirose et al. 2007) and a constant surface temperature 300K, the value of the maximum Carnot efficiency is between 0.93 and 0.92. Note that this estimate is solely derived just from the assumption of surface and core–mantle temperature. Like the Carnot efficiency, it provides a fundamental thermodynamic constraint that surprisingly does not involve assumptions about material parameters such as rheology and thermal material parameters or geometric characterizations. This defines an upper thermodynamic bound on the efficiency of heat transfer through a convecting mantle. The upper bound of the efficiency is commensurate with the lower bound of dissipation. All of the heat is available for work, there being no irreversible entropy production. In a self-driven heat engine ‘Earth’ the other extremum is the limit with zero efficiency. We discuss this case in figure 2a; all of the available high-grade heat is converted into low-grade heat at the surface temperature, and no work can be extracted. In this case, there would be no work available for mountain building or other plate tectonic phenomena observed near the surface.

These are the upper and lower bounds of irreversible entropy production in an Earth seen as a heat engine. A heat engine is a good abstraction for a cyclical process for which the planetary system is discussed as a whole and the cycle is defined by the overturn cycle of mantle convection. If we want to apply the thermodynamic approach in greater detail to geodynamic processes near the surface, we must consider non-cyclical deformation processes, steady-state deformation processes, where elasto-plastic deformation may be important.

An example would be a shear zone, in a solid, which may form at the top of the planet, in the lithosphere. These shear zones define plate boundaries and they persist over millions of years as deforming features. Geodynamic modelling
for these shear zones is based on laboratory measurements of elastic, plastic and steady-state creep components. The important property for defining a lower bound of dissipation is the yield threshold for transition from elastic to visco-plastic deformation. The classical lower and upper bound theorems from continuum mechanics may be used as a first pass to assess possible bounds of dissipation under the assumption of steady-state (quasi-static) deformation with no consideration of temperature feedback. Ziegler’s principle of maximum entropy production generalizes this framework to include other processes such as chemical processes. We have extended this classical framework through the consideration of temperature feedback. Our formulation coincides with the classical formulation if temperature is not considered.

10. Discussion

We have shown that thermodynamics provides an abstraction tool for assessing the validity of complex numerical simulations of the Earth. Thermodynamic limits can be used as a simple means to assess the validity of numerical simulations and thermodynamic approaches also provide indications on possible oversights in numerical approaches. A good example is the neglect of link between mechanical deformation and irreversible entropy production, i.e. the dissipation caused by shear heating in the mantle. Using the Boussinesq framework, it is possible to calculate efficiencies higher than the Carnot limit (Pons & Le Quere 2005). This is absolutely incompatible with basic thermodynamics. We have discussed here two bounds: maximum irreversible entropy production (convection with maximum irreversible entropy production) and the other extreme minimum irreversible entropy production (conduction). Both bounds are thermodynamically permissible. This example clearly highlights the importance of irreversible entropy production.

Another important stimulus provided by the thermodynamic approaches is to look at the Earth boundary conditions for the mantle convection simulations in a critical way. As the next level of refinement, a more realistic scenario is to consider the Earth not as an ideal Carnot heat engine but as the replacement of the boundaries with irreversible losses by an endoreversible engine in future numerical models. These endoreversible boundaries could be identified as the conductive lithosphere and the convective outer core (figure 3). For such an engine, the Carnot limit is much reduced. The endoreversible limit for an Earth with irreversible heat transfer losses with the environment is reduced to a value of $\eta_{\text{endo}} = 1 - \sqrt{T_{\text{surf}}/T_{\text{ICB}}}$ (Curzon & Ahlborn 1975). Again taking a surface temperature of 300 K and an inner core boundary temperature of $T_{\text{ICB}} = 5600$ K (Alfe et al. 2002), the efficiency of plate tectonics in an endoreversible Earth is thus reduced to $\eta_{\text{endo}} = 0.76$. Note that this estimate is solely derived just from the assumption of surface and inner core–outer core temperature as the boundary temperatures for the endoreversible boundaries. It provides a fundamental thermodynamic constraint that again does not involve assumptions about material parameters such as rheology and thermal material parameters or geometric characterizations. This value should not be violated by convection codes for the Earth mantle that are based on the endoreversible idealization.
Figure 3. A schematic diagram of the endoreversible engine identifying the irreversible losses at the upper boundary to the lithosphere and the irreversible losses at the lower boundary to the geodynamo.

Figure 4. A minimally dissipative mode of heat transfer from the core–mantle boundary temperature to the surface temperature with an affiliated lost work of $\eta_{2C} Q_{\text{cond}}$, where $\eta_{2C} = 1 - T_{\text{surf}}/T_{\text{core}}$ is the two-reservoir Carnot efficiency.

The next step of refinement for thermodynamic description of the Earth as a heat engine would be to include a parallel leaky wire (conduction) to the Curzon–Ahlborn engine as for the cases in figures 1, 2 and 4. This case has the interesting property that the maximum efficiency does not coincide with the maximum entropy production (Gordon & Huleihil 1992).

We believe that finite-time thermodynamics has a lot to offer to geodynamics through assessment of basic concepts such as thermodynamic length and constant thermodynamic speed. The concept of the following explicitly irreversible entropy
production has been specifically identified as one of the key problems to be solved in the science of unstable Earth phenomena such as earthquakes (Ben Zion 2008; Regenauer-Lieb & Yuen 2008), ice quakes and landslides (Regenauer-Lieb et al. 2009).

We have used mantle convection as the first example for the application of the extremum principles proposed here. Other simple applications that lend themselves to be interpreted by the Carnot analogy would be the geodynamo in the outer core (Stacey & Davis 2008). In our basic example for the Earth as a Carnot heat engine we have found that the assumption of minimum entropy production identifies the thermodynamic equilibrium system with minimally dissipative heat conduction. This is a possible solution for low heat input with subcritical Rayleigh number. However, when convection starts and reaches steady state the assumption of maximum entropy production provides an excellent upper bound of the mode of heat transfer. Without calculation of the critical Rayleigh number we are in no position to decide between the two extremes. Note that when the Rayleigh number is raised to the chaotic regime the notion of maximum entropy production as a good estimate of the heat transfer mode for steady state breaks down (Castillo & Hoover 1998). Time-dependent convective instabilities are also possible under lower Rayleigh numbers if highly non-linear rheologies are used (Moresi & Solomatov 1998). The upper and lower bounds provide a fundamental measure for predicting thermodynamically permissible bounds of steady-state convection calculations but should not be interpreted beyond steady state.

We conclude with the possible speculations on proposed limit theorems for other applications. The strongest result of this paper is the new extension of limit theorems in continuum mechanics, which are appended by the ones proposed here for entropy production. Future work will extend the concept for more realistic models of the Earth in terms of the analogy of an irreversible heat engine that will tighten the permissible bounds even further. We will also investigate the concept of time-dependent, irreversible entropy production for designing new thermodynamically based steady-state rheologies for use in geodynamics and continuum mechanics.

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